

**Evaluation of Reagents for the
Chemical Enhancement of
Fingermarks on Porous Surfaces:
Optimisation and
Characterisation of the
1,2-Indanedione Technique**

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This thesis is submitted in part fulfilment of the
requirements for a PhD in Science at the University of
Technology, Sydney

Thesis Submitted on 15th February 2008

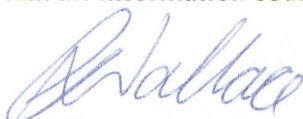
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Table of Contents

LIST OF FIGURES	v
LIST OF TABLES	xiii
LIST OF ABBREVIATIONS	xiv
ABSTRACT	xv
ACKNOWLEDGEMENTS	xviii
FOREWORDS	xix
Chapter 1: INTRODUCTION	1
1.1 INTRODUCTION TO FINGERMARKS	2
1.1.1 <i>The Value of Forensic Evidence and Fingerprint Evidence</i>	2
1.1.2 <i>The History of Fingermarks</i>	2
1.1.3 <i>General Fingerprints</i>	4
1.1.4 <i>Fingerprint Identification and Classification</i>	4
1.2 THE DETECTION OF FINGERMARKS	7
1.2.1 <i>Fingermark Detection</i>	7
1.2.2 <i>Development of Latent Fingermarks for Porous Surfaces</i>	8
1.3 FINGERMARK REAGENTS ON POROUS SURFACES	11
1.3.1 <i>New Fingermark Reagents for Porous Surfaces</i>	11
1.4 1,2-INDANEDIONE	12
1.4.1 <i>History of 1,2-Indanedione as a Fingermark Reagent</i>	12
1.4.2 <i>Sequencing</i>	13
1.4.3 <i>Detection Methods for Chemically Enhanced Latent Fingermarks on Paper</i>	13
1.4.3.1 <i>Forensic Light Sources</i>	14
1.4.3.2 <i>Chemical Imaging</i>	14
1.5 5-METHYLTHIONINHYDRIN	15
1.6 THE DEVELOPMENT OF FINGERMARKS ON THERMAL PAPER	15
1.7 CHARACTERISATION OF THE PRODUCT OF AMINO OF AMINO ACIDS AND FINGERMARK REAGENTS	16
1.7.1 <i>Ninhydrin</i>	16
1.7.2 <i>DFO</i>	17
1.7.3 <i>1,2-Indanedione</i>	18
Chapter 2: FINGERPRINTS ON POROUS SURFACES – A SURVEY	21
2.1 INTRODUCTION	22
2.2 MATERIALS AND METHODS	23
2.3 RESULTS	23
2.4 DISCUSSION	31
2.5 CONCLUSION	34
Chapter 3: OPTIMISATION OF 1,2-INDANEDIONE	35
3.1 INTRODUCTION	36
3.2 GENERAL MATERIALS AND METHODS	38
3.2.1 <i>Selection of Support Samples</i>	38
3.2.2 <i>Preparation of Latent Fingermark Samples</i>	39
3.3 1,2-INDANEDIONE FORMULATIONS	40
3.3.1 <i>Introduction</i>	40
3.3.2 <i>Materials and Methods</i>	40
3.3.2.1 <i>1,2-Indanedione Formulations</i>	40
3.3.2.2 <i>Development Conditions</i>	42
3.3.2.3 <i>Method Of Detection</i>	42
3.3.2.4 <i>Optimisation of Carrier Solvent</i>	43
3.3.3 <i>Results</i>	43
3.3.3.1 <i>1,2-Indanedione Formulations</i>	43
3.3.3.2 <i>Direct Comparison of Formulation 3 and Formulation 4</i>	46
3.3.3.3 <i>Optimisation of Carrier Solvent for Formulation 4</i>	46
3.3.3.4 <i>Summary of Formulation Comparison</i>	49
3.3.4 <i>Discussion</i>	50
3.3.4.1 <i>Stability Problems of Formulations</i>	50
3.3.4.2 <i>Optimisation of Formulations</i>	50
3.3.4.3 <i>Optimisation of Carrier Solvents</i>	51
3.3.5 <i>Conclusion</i>	52
3.4 COMPARISON OF CASALI INSTITUTE 1,2-INDANEDIONE AND BVDA 1,2-INDANEDIONE	52
3.4.1 <i>Introduction</i>	52
3.4.2 <i>Materials and Methods</i>	53
3.4.2.1 <i>Visual Comparison</i>	53
3.4.2.2 <i>Comparison of Fingermarks</i>	53

4.4.4 Discussion	93
4.4.5 Conclusion	93
4.5 DEVELOPMENT OF FINGERMARKS ON DIFFICULT BACKGROUNDS AND SURFACES USING 1,2-INDANEDIONE	93
4.5.1 Introduction	93
4.5.2 Materials and Methods	95
4.5.3 Results	94
4.5.4 Discussion	97
4.5.5 Conclusion	97
4.6 ZINC METAL SALT TREATMENT STUDY	98
4.6.1 Introduction	98
4.6.2 Materials and Methods	99
4.6.3 Results	100
4.6.4 Discussion	103
4.6.5 Conclusion	105
Chapter 5: A STUDY OF THE 1,2-INDANEDIONE/ AMINO ACID REACTION	106
5.1 AMINO ACID REAGENTS – GENERAL INTRODUCTION	107
5.1.1 1,2-Indanedione	110
5.1.2 Characterisation of 1,2-Indanedione	112
5.2 MATERIALS AND METHODS	112
5.2.1 General Instrumentation	112
5.2.1.1 Chromatography	112
5.2.1.2 UV-Visible Spectroscopy (UV-Vis)	113
5.2.1.3 Fluorescence Spectroscopy	115
5.2.1.4 Mass Spectrometry	116
5.2.1.5 Infrared Spectroscopy	117
5.2.1.6 Nuclear Magnetic Resonance Spectroscopy (NMR)	118
5.2.1.7 Thermal Analysis	119
5.2.1.8 Elemental Analysis	119
5.2.2 General Experimental Methods	119
5.2.3 Investigation of Some Properties of 1,2-Indanedione	120
5.2.4 Colour and Fluorescence Spectroscopy Study	121
5.2.5 Preliminary Study of the Reaction between 1,2-Indanedione and Amino Acids (Part A)	122
5.2.5.1 Materials	122
5.2.5.2 Heating under Reflux	122
5.2.5.3 Reduced Heating with Acid	122
5.2.5.4 Reduced Heating without Acid	123
5.2.5.5 Reaction without Heat	123
5.2.5.6 Limited Reaction by Quenching	123
5.2.5.7 UV-Visible Spectroscopy Study of 1,2-Indanedione and Amino Acid Products	124
5.2.6 A Further Study of the Reaction between 1,2-Indanedione and Amino Acids (Part B)	124
5.2.6.1 Study of the R Group of the Amino Acid	124
5.2.6.2 Temperature and Time Study	125
5.2.6.3 Water Content	126
5.2.6.4 Study by Solid Nuclear Magnetic Resonance Spectroscopy	126
5.2.6.5 Free Radical Study on the Product of 1,2-Indanedione and Alanine	127
5.2.6.6 Thermal Analysis	127
5.2.6.7 Elemental Analysis	128
5.2.7 Study of the Reaction between 1,2-Indanedione, Amino Acids and Metal Salts (Part C)	128
5.3 RESULTS AND DISCUSSION	129
5.3.1 Investigation of Some Properties of 1,2-Indanedione	129
5.3.1.1 Electrospray Mass Spectroscopy	129
5.3.1.2 Nuclear Magnetic Resonance Spectroscopy	130
5.3.2 Colour and Fluorescence Spectroscopy of 1,2-Indanedione and Amino Acids	134
5.3.3 Preliminary Study of the Reaction between 1,2-Indanedione and Amino Acids (Part A)	137
5.3.3.1 Heating under Reflux and Lowering the Temperature with and without Acid	137
5.3.3.2 Reaction without Heat	139
5.3.3.3 Analysis of the reaction Products by Instrumental Analysis	141
5.3.3.4 Summary of Part A of the Study of 1,2-Indanedione and Amino Acids	145
5.3.4 A Further Study of the Reaction between 1,2-Indanedione and Amino Acids (Part B)	146
5.3.4.1 Study of the R Group of the Amino Acid	146
5.3.4.2 Study of the Effect of Water Content on the 1,2-Indanedione and Alanine Reaction	152
5.3.4.3 Solid NMR Study of the Product of 1,2-Indanedione and Alanine	153
5.3.4.4 Free Radical Study of the Product of 1,2-Indanedione and Alanine	155
5.3.4.5 Thermal Analysis	155
5.3.4.6 Elemental Analysis	157
5.3.4.7 Summary of the Study of the 1,2-Indanedione and Amino Acids (Part B)	157
5.3.5 Preliminary Study of the Reaction between 1,2-Indanedione, Amino Acids and Metal Salts (Part C)	158
5.3.5.1 Metal Salt Reaction Preparation	158

5.3.5.2 UV-Visible Spectroscopy	159
5.3.5.3 Electrospray Mass Spectroscopy	160
5.3.5.4 Nuclear Magnetic Resonance Spectroscopy	163
5.3.5.5 Infrared Spectroscopy	164
5.3.5.6 Summary of the Study of the Reaction Product of 1,2-Indanedione, Amino Acids and Metal Salts	166
5.4 CONCLUSION	167
Chapter 6: OTHER APPLICATIONS FOR FINGERMARK DEVELOPMENT ON POROUS SURFACES	169
6.1 5-METHYLTHIONINHYDRIN	170
6.1.1 Introduction	170
6.1.2 Materials and Methods	171
6.1.2.1 Reagents	171
6.1.2.2 Preparation of Latent Fingermark Samples	171
6.1.2.3 Carrier Solvent Study	171
6.1.2.4 Comparison with Conventional Reagents	172
6.1.2.5 Spectroscopy Study	173
6.1.2.6 Price Comparison	173
6.1.3 Results and Discussion	173
6.1.3.1 Carrier Solvent Study	173
6.1.3.2 Comparison to Conventional Reagents	175
6.1.3.3 Price Comparison	181
6.1.3.4 General Discussion	181
6.1.4 Conclusion	182
6.2 THE DEVELOPMENT OF FINGERMARKS ON THERMAL PAPER	182
6.2.1 Introduction to Thermal Paper	182
6.2.1.1 Composition	182
6.2.1.2 Printing Mechanism	185
6.2.1.3 The Problem of Developing Fingermarks on Thermal Paper	185
6.2.1.4 Introduction to Research that has been Performed on Thermal Paper	186
6.2.2 Materials and Methods	188
6.2.2.1 General Materials and Methods Reagents	188
6.2.2.2 Application, Development and Evaluation of Solutions	189
6.2.2.3 Evaluation of Samples Developed	189
6.2.2.4 Part 1: Evaluation of all Techniques on Thermal Paper	190
6.2.2.5 Evaluation of the Best Techniques on Different Thermal Paper	191
6.2.2.6 Evaluation of Novel Ind-dry Method	191
6.2.3 Results and Discussion	192
6.2.3.1 Evaluation of Different Carrier Solvents for Thermanin	192
6.2.3.2 Development of Fingermarks	193
6.2.3.3 Second Evaluation on Multiple Types of Thermal Paper	198
6.2.3.3.1 Latent Fingermarks and Background	198
6.2.3.3.2 Summary of Results	201
6.2.3.4 Enhancing Solution Sensitivity with Acetic Acid	202
6.2.3.5 Novel Method for Thermal Paper Treatment – Ind-dry	203
6.2.3.6 Price Comparison	204
6.2.3.7 General Discussion	205
6.2.4 Conclusion	206
Chapter 7: GENERAL CONCLUSIONS AND RECOMMENDATIONS FOR FURTHER RESEARCH	207
7.1 Fingermarks on Porous Surfaces – A Survey	208
7.2 Optimisation of 1,2-Indanedione	209
7.3 Applications of 1,2-Indanedione	210
7.4 Characterisation of the 1,2-Indanedione Technique	211
7.5 Other Applications for the Development of Fingermarks on Porous Surfaces	213
7.6 General Conclusions	214
References	215
Appendix A: THESIS PAPERS	230
Appendix B: SURVEY – FINGERPRINTS ON POROUS SURFACES	233
Appendix C: FINGERMARK REAGENT FORMULATIONS	236

LIST OF FIGURES

Figure 1.1 – Level 1 detail - Arch pattern (Dalrymple, 2000)	4
Figure 1.2 – Level 1 detail - Loop pattern (Dalrymple, 2000)	4
Figure 1.3 – Level 1 detail - Double loop pattern (Dalrymple, 2000)	5
Figure 1.4 – Level 1 detail - Whorl pattern (Dalrymple, 2000)	5
Figure 1.5 – Level 2 detail – Minutiae (Dalrymple, 2000)	5
Figure 1.6 – Level 3 detail – Pores located along the ridges of the fingermark (Barclay, 1991)	6
Figure 1.7 - Treatment sequence for fingermarks on porous surfaces (adapted from Stoilovic and Lennard, 2000)	9
Figure. 1.8 – Chemical structure of 1,8-diaza-9-fluorenone (DFO) (Grigg <i>et al.</i> , 1990)	10
Figure 1.9 – Chemical structure of ninhydrin (Ruhemann, 1910)	10
Figure 1.10 – The reaction between ninhydrin and an amino acid to form Ruhemann's purple	10
Figure 1.11 – Chemical structure of 1,2-indanedione	11
Figure 1.12 – Chemical structure of 5-methylthioninhydrin	12
Figure 1.13 – Chemical structure of zinc metal complex	17
Figure 1.14 – Reaction of DFO with amino acids (Grigg <i>et al.</i> , 1990)	17
Figure 1.15 – Reaction mechanism of DFO and l-alanine (Wilkinson, 2000)	18
Figure 1.16 - Proposed reaction mechanism of 1,2-indanedione with amino acids (Petrovskaia <i>et al.</i> , 2001)	19
Figure 1.17 - Suggested complex formed by the reaction of amino acids with 1,2-indanedione (Petrovskaia <i>et al.</i> , 2001)	20
Figure 2.1 – Survey respondents by origin of country	24
Figure 2.2 - Percentage of fingerprint laboratories that use the specified reagents for the treatment of porous surface exhibits	25
Figure 2.3 – Frequency of use of specified reagents (ninhydrin, DFO and physical developer) in casework	26
Figure 2.4 – 1,2-Indanedione relative awareness and experience among survey respondents	29
Figure 2.5 – Relative willingness of laboratories to incorporate 1,2-indanedione into the reagent repertoire	31
Figure 3.1 – Schematic of layout of fingermark samples on paper	39
Figure 3.2 – Locations of cuts on fingermark samples on paper	40
Figure 3.3 – (Top Row) All fingermarks were 1 month old and viewed under white light using the VSC 2000. (Bottom Row) All fingermarks were 1 month old and viewed in the fluorescence mode (Exc.440-580 nm, Em. 610-630 nm) using the VSC 2000	44
Figure 3.4 – 1 week old fingermark treated with formulation 3 and viewed in absorption mode	45

Figure 3.5 – Fingerprint developed with - Formulation 3 (left): Formulation 4 (right) viewed in absorption mode	46
Figure 3.6 – Fingerprint developed with - Formulation 3 (left): Formulation 4 (right) viewed in fluorescence mode	46
Figure 3.7 – 9 month old fingerprint HFE 71de solvent (left) HFE 7100 solvent (right) viewed under white light	48
Figure 3.8 – 9 month old fingerprint HFE 71de solvent (left): HFE 7100 solvent (right) viewed in fluorescence mode	48
Figure 3.9 – 9 month old fingerprint HFE 71de solvent (left): HFE 7100 solvent (right) viewed under white light	48
Figure 3.10 – 9 month old fingerprint HFE 71de solvent (left):HFE 7100 solvent (right) viewed in fluorescence mode	48
Figure 3.11 – BVDA 1,2-indanedione received in early 2003	53
Figure 3.12 – BVDA 1,2-indanedione received in mid 2005	53
Figure 3.13 – Casali Institute 1,2-indanedione received in mid 2005	53
Figure 3.14 – Fingermarks developed with 1,2-indanedione Casali Institute (Australian formulation) (left): BVDA (Australian formulation) (right) viewed on the VSC 2000. Exc: 440-580 nm, Em: 610 nm	54
Figure 3.15 – Fingermarks developed with 1,2-indanedione Casali Institute (Israeli formulation) (left): BVDA (Australian formulation) (right) viewed on the VSC 2000. Exc: 440-580 nm, Em: 610 nm	55
Figure 3.16 – Fingermarks developed with DFO (left): Casali Institute 1,2-indanedione (Australian formulation) (right) viewed on the VSC 2000. Exc: 440-580 nm, Em: 610 nm	55
Figure 3.17 – 1 month old mark treated with Formulation 3 and developed with the heat press. Viewed in absorption mode.	61
Figure 3.18 – 1 month old mark treated with Formulation 3 and developed with the heat press. Viewed in absorption mode	61
Figure 3.19 – 1 month old mark treated with Formulation 3 and developed with the heat press. Viewed in fluorescence mode.	61
Figure 3.20 – The Video Spectral Comparator 2000 by Forster and Freeman	64
Figure 3.21 – The Polilight by Rofin, Australia	65
Figure 3.22 – Barrier filters and band positions of the Polilight PL10 (Adapted from Stoilovic and Lennard, 2005)	66
Figure 3.23 – Sample array at individual wavelengths. Grey squares indicate the same pixel at each individual wavelength that are combined to form a spectrum (Adapted from Exline, 2003)	67
Figure 3.24 – The process of Chemical Imaging, a combination of spectroscopy and digital imaging (Adapted from Treado, 1995)	68
Figure 3.25 – The Condor Chemical Imaging microscope (Chemimage, 2001)	68

Figure 3.26 – The Condor Chemical Imaging microscope (Chemimage, 2001)	68
Figure 3.27 – Front of the bank deposit slip	72
Figure 3.28 – Back of the bank deposit slip	72
Figure 3.29 – Fingermark developed with 1,2-indanedione on the back of the bank deposit slip	72
Figure 3.30 – Front of Vodaphone prepaid receipt	73
Figure 3.31 – Fingermark developed on the front of Vodaphone receipt	73
Figure 3.32 – Fingermark developed on the front of Vodaphone receipt	73
Figure 3.33 – Front of threatening letter left on victims vehicle	74
Figure 3.34 – Back of threatening letter left on victims vehicle	74
Figure 3.35 – Fingermark developed with 1,2-indanedione on the back of letter	74
 Figure 4.1 – Chemical structure of 1,8-diaza-9-fluorenone (DFO)	 76
Figure 4.2 – Chemical structure of ninhydrin	76
Figure 4.3 – Sensitivity of reagent concentration grid (glycine concentrations specified)	77
Figure 4.4 – 8 month old fingermark treated with 1,2-indanedione (left) and ninhydrin (right) viewed under white light	81
Figure 4.5 – 8 month old fingermark treated with ninhydrin (left) and 1,2-indanedione (right) viewed under white light	81
Figure 4.6 – 3 month old fingermark treated with 1,2-indanedione (left) and zinc metal salt post ninhydrin treatment (right). Viewed in fluorescence mode	82
Figure 4.7 – 3 month old fingermark treated with zinc metal salt post ninhydrin treatment (left) and 1,2-indanedione (right) and cooled with liquid nitrogen. Viewed in fluorescence mode	82
Figure 4.8 – 8 month old fingermark treated with 1,2-indanedione (left) and cadmium metal salt post ninhydrin treatment (right) and cooled with liquid nitrogen. Viewed in fluorescence mode	83
Figure 4.9 – 8 month old fingermark treated with 1,2-indanedione (left) and cadmium metal salt post ninhydrin treatment (right) and cooled with liquid nitrogen Viewed in fluorescence mode	83
Figure 4.10 – Fresh fingermarks treated with 1,2-indanedione (left) and AFP DFO formulation (right). Exc: 530 nm, Det:590 nm	83
Figure 4.11 – Fresh fingermark treated with DFO (left): 1,2-indanedione (right). Exc:440-480 nm, Det:610 nm	84
Figure 4.12 – Fresh fingermark treated with 1,2-indanedione (left): DFO (right) Exc: 440-480 nm, Det:610 nm	84
Figure 4.13 – 9 month old fingermark treated with 1,2-indanedione (left): DFO (right) viewed under white light	84

Figure 4.14 – 9 month old fingermark treated with AFP DFO formulation (left) and HOSDB DFO formulation (right) Exc:440-480 nm, Det:610 nm	85
Figure 4.15 – 9 month old fingermark treated with HOSDB DFO formulation (left) and 1,2-indanedione (right) Exc:440-480 nm, Det:610 nm	85
Figure 4.16 – 9 month old fingermark treated with HOSDB DFO formulation (left) and 1,2-indanedione formulation (right) Exc:440-480 nm, Det:610 nm	85
Figure 4.17 – 9 month old fingermark treated with HOSDB DFO formulation (left) and 1,2-indanedione formulation (right) Exc:440-480 nm, Det:610 nm	85
Figure 4.18 – 9 month old fingermark treated with 1,2-indanedione (left) and HOSDB DFO formulation (right) Exc:440-480 nm, Det:610 nm	86
Figure 4.19 – 9 month old fingermark treated with HOSDB DFO formulation (left) and 1,2-indanedione formulation (right) Exc:440-480 nm, Det:610 nm	86
Figure 4.20 – Fingermarks treated with a sequence of 1,2-indanedione followed by ninhydrin and captured under white light	88
Figure 4.21 – Fingermarks treated with a sequence of 1,2-indanedione followed by ninhydrin and captured under white light	88
Figure 4.22 – Fingermark on receipt paper viewed under white light	95
Figure 4.23 – Fingermark on yellow envelope viewed under white light	95
Figure 4.24 – Fingermark on white envelope viewed under white light	95
Figure 4.25 – Fingermark on yellow envelope, Exc:440-480 nm, Det:610 nm	96
Figure 4.26 – Fingermark on facsimile paper, Exc:440-480 nm, Det:610 nm	96
Figure 4.27 – Fingermark on fluorescent green paper, Exc:440-480 nm, Det:610 nm	96
Figure 4.28 – Wallpaper viewed under white light	96
Figure 4.29 – Fingermark developed on wallpaper and viewed using a Polilight. Exc: 530 nm, Em: 590 nm. Captured using a Nikon F90	96
Figure 4.30 – Fingermark developed on raw wood and viewed under white light	97
Figure 4.31 – Fingermark developed on raw wood and viewed using a Polilight. Exc: 530 nm, Em: 590 nm. Captured using a Nikon F90	97
Figure 4.32 – Fingermarks developed on recycled paper in Canberra with 1,2-indanedione and steam (left): 1,2-indanedione (right) under white light	100
Figure 4.33 – Fingermarks developed in Sydney with IndZn (left): 1,2-indanedione (right) under white light	101
Figure 4.34 – Fingermarks developed in Sydney with IndZn (left): 1,2-indanedione (right). Exc:530 nm Em: 590 nm	101
Figure 4.35 – Fingermarks developed in Canberra with 1,2-indanedione (left): IndZn (right) under white light	101
Figure 4.36 – Fingermarks developed in Canberra with 1,2-indanedione (left): IndZn (right). Exc:530 nm Em: 590 nm	101

Figure 4.37 – Fingermarks developed in Sydney with 1,2-indanedione plus zinc (left): IndZn (right) under white light	102
Figure 4.38 – Fingermarks developed in Sydney with IndZn (left): 1,2-indanedione plus zinc (right). Exc:530 nm Em: 590 nm	102
Figure 4.39 – Fingermarks developed in Canberra with 1,2-indanedione plus zinc (left): IndZn (right) under white light	102
Figure 4.40 – Fingermarks developed in Canberra with 1,2-indanedione plus zinc (left): IndZn (right). Exc:530 nm Em: 590 nm	102
Figure 4.41 – Fingermarks developed in Sydney with IndZn (left): IndZn plus steam (right) under white light	103
Figure 4.42 – Fingermarks developed in Sydney with IndZn (left): IndZn plus steam (right). Exc:530 nm Em: 590nm	103
Figure 4.43 – Fingermarks developed in Canberra with IndZn plus steam (left): IndZn (right) under white light	103
Figure 4.44 – Fingermarks developed in Canberra with IndZn plus steam (left): IndZn (right) Exc:530 nm Em: 590 nm	103
Figure 5.1 – Chemical structure of Ruhemann's purple	107
Figure 5.2 – Reaction mechanism of ninhydrin with amino acids (Wilkinson, 2000)	107
Figure 5.3 – Metal salt – Ruhemann's purple complex (Lennard 1986)	108
Figure 5.4 – Chemical structure of ascorbic acid	110
Figure 5.5 – Chemical structure of dehydroascorbic acid	110
Figure 5.6 – Possible pathways of 1,2-indanedione reaction with two possible sites of attack (Taylor, 2001)	110
Figure 5.7 – Repeating unit m/z 146 (Mills, 2004)	111
Figure 5.8 – Repeating unit m/z 146 (Mills, 2004)	111
Figure 5.9 – Schematic of a standard UV-Visible spectrometer (http://www.cem.msu.edu/~reusch/VirtualText/Spectrpy/UV-Vis/uvspec.htm accessed 9/2/2005)	114
Figure 5.10 – Carey 3E UV-Visible spectrometer	114
Figure 5.11 – LS50 Perkin Elmer spectrometer	115
Figure 5.12 – Standard electrospray ionisation source (Burkitt <i>et. al.</i> , 2003)	116
Figure 5.13 – Electrospray ionisation mass spectrometer	117
Figure 5.14 – Nicolet Magna infrared spectrometer	117
Figure 5.15 – Bruker DRX 300 MHz nuclear magnetic resonance spectrometer	118
Figure 5.16 – Schematic diagram of an elemental analyser	119
Figure 5.17 – Chemical structure of alanine	125
Figure 5.18 – Chemical structure of cysteine	125
Figure 5.19 – Chemical structure of urea	125

Figure 5.20 – Chemical structure of proline	125
Figure 5.21 – Electrospray mass spectrum of Casali Institute 1,2-indanedione	129
Figure 5.22 – Electrospray mass spectrum of BVDA 1,2-indanedione	130
Figure 5.23 – ^1H -NMR spectrum of BVDA 1,2-indanedione in CDCl_3	131
Figure 5.24 – Expansion of ^1H NMR spectrum of BVDA 1,2-indanedione in CDCl_3	131
Figure 5.25 – ^1H Chemical shifts of 1,2-indanedione	132
Figure 5.26 – ^{13}C -NMR spectra of Casali 1,2-indanedione	133
Figure 5.27 – Expansion of ^{13}C -NMR spectrum of Casali 1,2-indanedione	133
Figure 5.28 – Fluorescence spectra for the reaction product formed between glycine and 1,2-indanedione, recorded at room temperature: 1. Excitation; 2 Emission	135
Figure 5.29 – Fluorescence spectra for the reaction product formed between glycine and 1,2-indandione followed by zinc metal, recorded at room temperature 1. Excitation; 2 Emission	136
Figure 5.30 – Product of 1,2-indanedione and alanine in a round bottom flask	140
Figure 5.31 – Product of 1,2-indanedione and glycine in a round bottom flask	140
Figure 5.32 – Electrospray mass spectrum of the 1,2-indanedione and alanine product indicating oligomer formation	141
Figure 5.33 – Electrospray mass spectrum of 1,2-indanedione and alanine quenched for 5 minutes using a dry ice bath	142
Figure 5.34 - Infrared spectrum of the product formed between 1,2-indanedione and alanine	143
Figure 5.35 - UV-Visible spectrum of 1,2-indanedione and alanine in different solvents (time = 1 hour)	144
Figure 5.36 – Electrospray mass spectrum of the 1,2-indanedione and alanine reaction quenched after 1 minute	147
Figure 5.37 – Electrospray mass spectrum of the 1,2-indanedione and cysteine reaction quenched after 1 minute	147
Figure 5.38 – Proposed mass fragments for the 1,2-indanedione and alanine reaction mixture	148
Figure 5.39 – Proposed mass fragments for the 1,2-indanedione and cysteine reaction mixture	149
Figure 5.40 – Electrospray mass spectrum for the 1,2-indanedione and proline reaction mixture quenched after 1 minute	150
Figure 5.41 – Proposed mass fragments for the 1,2-indanedione and proline reaction mixture	151
Figure 5.42 – ^{13}C Solid NMR spectra of the 1,2-indanedione and alanine reaction product	154
Figure 5.43 – Proposed structure of the main reaction product of 1,2-indanedione and alanine	155
Figure 5.44 – TGA-DTA curve for the 1,2-indanedione and alanine reaction mixture	156
Figure 5.45 – Product of 1,2-indanedione, alanine and zinc metal salt in solution	158
Figure 5.46 – Solid product of 1,2-indanedione, alanine and zinc metal salt	158
Figure 5.47 – UV-Visible spectra recorded for a mixture of 1,2-indanedione, alanine and zinc chloride in n-propanol. The reaction was monitored over a 24-hour period. The reaction was monitored over a 24-hour period. Spectra labelled 1,2-indanedione	

+ alanine at time = 0 and reaction after 24 hours. Each spectrum in between shows the general progression from time = 0 to time = 24 hours	160
Figure 5.48 - Mass spectrum of the reaction product of 1,2-indanedione with alanine and zinc chloride	161
Figure 5.49 - Mass spectrum of the reaction product of 1,2-indanedione with alanine and cadmium nitrate	162
Figure 5.50 - Nuclear Proton nuclear magnetic resonance spectra: (1) 1,2-indanedione, (2) 1,2-indanedione and alanine, and (3) 1,2-indanedione, alanine and zinc metal salt	163
Figure 5.51 - Infrared spectrum of the reaction products of 1,2-indanedione with alanine and zinc chloride	164
Figure 5.52 - Infrared spectrum of the reaction products of 1,2-indanedione with alanine and cadmium nitrate	165
Figure 6.1 - Chemical structure of 5-methylthioninhydrin	170
Figure 6.2 - Comparison of 5-MTN in HFC 4310mee (left) and petroleum ether (right) carrier solvents. Viewed using white light and photographed using a Nikon F90 camera and Fuji 400 speed photographic film	174
Figure 6.3 - Comparison of 5-MTN in HFE 7100(left) and petroleum ether (right) carrier solvents. Viewed using white light and photographed using a Nikon F90 camera and Fuji 400 speed photographic film	174
Figure 6.4 - Comparison of 5-MTN (left) and ninhydrin (right), viewed using white light and photographed using a Nikon F90 camera and Fuji 400 speed photographic film	176
Figure 6.5 - Comparison of ninhydrin (left) and 5-MTN (right), viewed using white light and photographed using a Nikon F90 camera and Fuji 400 speed photographic film	176
Figure 6.6 - Comparison of 5-MTN (left) and ninhydrin (right) after metal salt treatment; viewed at room temperature using Polilight excitation at 505 nm and viewing through an KV 550 nm filter. Photographed using a Nikon F90 camera and Fuji 400 speed photographic film	177
Figure 6.7 - Comparison of 5-MTN (left) and 1,2-indanedione (right). Viewed at room temperature using Polilight excitation at 530 nm and viewing through an OG 590 nm barrier filter. Photographed using a Nikon F90 camera and Fuji 400 speed photographic film	178
Figure 6.8 - Absorption spectra for fingerprints treated with 5-MTN 1. Fingerprint developed with 5-MTN; 2. Fingerprint developed with 5-MTN and cadmium metal salt; 3. Fingerprint developed with 5-MTN and zinc metal salt	179
Figure 6.9 - 1. Emission spectra of a fingerprint treated with 5-MTN and zinc metal salt at room temperature. Excitation slit = 15 nm; Emission slit = 5 nm; λ_{ex} = 500 nm; 2. Excitation spectra of a fingerprint treated with 5-MTN and zinc metal salt at room temperature. Excitation slit = 5 nm; Emission slit = 15 nm; λ_{em} = 620 nm	180
Figure 6.10 - Layers of thermal paper (Pasquier, 2005)	183

Figure 6.11 – An example of a developer: Phenol, 4,4'-(1-methylethylidene)bis	183
Figure 6.12 – Example of reaction creating colour in the active layer (Truffi, 2000)	184
Figure 6.13 – An example of an activator: Ethylene glycol diphenyl ether	184
Figure 6.14 – Ninhydrin derivative from 3,5,5-trimethyl-1-hexanol	186
Figure 6.15 – Evaluation scheme used for the evaluation of revealed fingerprints	190
Figure 6.16 – Fingerprint developed on active side with “nin-dry”. Viewed under white light	195
Figure 6.17 - Same fingerprint, enhanced contrast with Adobe® Photoshop®	195
Figure 6.18- Fingerprint developed on active side with NFTP. Viewed under white light	196
Figure 6.19 - Same fingerprint, enhanced contrast with Adobe® Photoshop®	196
Figure 6.20 – Fingerprint developed on active side with 1,2-indanedione. Excited at 530 nm, observed at 550 nm	196
Figure 6.21 – Same fingerprint as figure 6.20, inverted contrast with Adobe® Photoshop®	196
Figure 6.22 – Processed paper treated with Thermanin in cyclohexane	197
Figure 6.23 – A depleted fingerprint developed on active side with Thermanin in HFE-7100	197
Figure 6.24 – Same fingerprint, enhanced contrast with Adobe® Photoshop®	197
Figure 6.25 – 3 rd depletion fingerprint developed on active side with 1,2-indanedione. Excited at 530 nm, observed at 550 nm	199
Figure 6.26 – Same fingerprint, as figure 6.25 inverted contrast with Adobe® Photoshop®	199
Figure 6.27 – 3 rd depletion fingerprint developed on active side with Thermanin in HFE 7100	200
Figure 6.28 – Same fingerprint as figure 6.27, enhanced contrast with Adobe® Photoshop®	200
Figure 6.29 – Background noise created on a sample treated with Thermanin in pentane	200
Figure 6.30 – Darkening of the active layer on a sample treated with Thermanin in petroleum ether	200
Figure 6.31 – Effect on the active layer of a solution of 1,2-indandione with 0.5% acetic acid	202
Figure 6.32 – Fingerprint developed with Ind-dry(left) and 1,2-indanedione (right). Viewed using 530 nm excitation and 550nm observation	203
Figure 6.33 – 1,2-Indanedione developed fingerprint on a receipt. Viewed using 530 nm excitation and 550 nm observation	204

LIST OF TABLES

Table 1.1 - Main constituents of gland secretions commonly found in latent fingerprints (Knowles, 1978)	8
Table 2.1 – Ninhydrin formulations	27
Table 2.2 – DFO formulations	27
Table 2.3 – 1,2-Indanedione formulations	28
Table 3.1 – Surfaces used for the comparison of 1,2-indanedione formulations	38
Table 3.2 – Chemical properties of carrier solvents	47
Table 3.3 – Summary of results of all 1,2-indanedione formulations	49
Table 3.4 – Results of temperature analysis of heat press settings	59
Table 3.5 – Specifications of instruments used for detection	69
Table 4.1 – Sensitivity of 1,2-indanedione compared with conventional reagents and treatments using the amino acid glycine (figures indicate lowest concentration of glycine detected)	78
Table 4.2 – Results of the analysis of A4 student examination sheets	90
Table 4.3 – Price comparison of fingermark reagents	92
Table 4.4 – Various background supports for 1,2-indanedione evaluation	94
Table 5.1 – Content of water contained in each experiment	126
Table 5.2 – Results of reaction between amino acids, 1,2-indanedione and metal salts on filter paper	134
Table 5.3 – Comparison of the peaks and assignments of the infrared spectrum of the 1,2-indanedione product with Ruhemann's purple	143
Table 5.4 – Physical appearance of different amino acids and urea when reacted with 1,2-indanedione at different temperatures	146
Table 5.5 - Water content versus the colour, over time, for the 1,2-indanedione and alanine reaction	152
Table 5.6 – Table of the ^{13}C environment assignments for the peaks observed in the solution and solid state NMR spectra for the 1,2-indanedione and alanine reaction product	154
Table 5.7 – Comparison of the peaks and assignments for the infrared spectra recorded for the zinc metal salt complex, the cadmium metal salt complex and the 1,2-indanedione/ alanine product	165
Table 6.1 – Origin of samples used as substrates in part II	191
Table 6.2 – Summary of results from part I on processed paper	193
Table 6.3 – Summary of results from part I on non-processed paper	194
Table 6.4 – Summary of Results on Thermal Paper	201
Table 6.5 – Price comparison of reagents for thermal paper	204

List of Abbreviations

ACT – Australian Capital Territory
 AFP – Australian Federal Police
 CFC – Chlorofluorocarbons
 CI – Chemical Imaging
 CPMAS – Cross Polarization Magic Angle Spinning
 DFO – 1,2-diazofluorenone
 DIFS – Division of Identification and Forensic Science (Israel Police)
 DMSO – Dimethyl sulfoxide
 DSC – Differential Scanning Curves
 DTG – Derivative Thermogravimetry
 ESMS – Electrospray Mass Spectrometry
 FBI – Federal Bureau of Investigations
 FLS – Forensic Light Source
 ENFSI – European Network Of Forensic Science Institutes
 HFC 4310mee – 1,1,1,2,3,4,4,5,5,5-decafluoropentane
 HFE 7100 – 1-methoxynonafluorobutane
 HFE 71de – 1-methoxynonafluorobutane and 1,2-dichloroethylene
 HOSDB – Home Office Scientific Development Branch
 IAI – International Association for Identification
 IFRG – International Fingerprint Research Group
 IND – 1,2-Indanedione
 INDZN – Formulation of 1,2-Indanedione containing zinc
 IR – Infrared
 LCTF – Liquid Crystal Tuneable Filter
 MS – Mass Spectrometry
 NMR – Nuclear Magnetic Resonance
 SWGFAST – Scientific Working Group Friction Ridge Analysis, Study and Technology
 TGA – Thermogravimetric Analysis
 TLC – Thin Layer Chromatography
 USSS – United States Secret Service
 UTS – University of Technology, Sydney
 UV-VIS – Ultraviolet – Visible
 VSC 2000 – Video Spectral Comparator 2000

ABSTRACT

There is a continual search for new and improved reagents to detect fingerprints on a variety of surfaces. With increased technology and resources the possibilities are continually expanding. 1,2-Indanedione is a relatively new reagent for the development of fingerprints on porous surfaces. Its boundaries have not been completely explored nor has the method of reaction with fingerprints been determined. The initial aim of this project was to investigate the fingerprint reagent 1,2-indanedione and determine if it was a viable reagent for routine use in Australia. The secondary aim was to study the reaction that occurs between 1,2-indanedione and amino acids and the subsequent reaction with metal salts to gain further insight into the reaction than has been previously published. Additionally the fingerprint reagent 5-methylthioninhydrin, which although had shown good results in detecting fingerprints in the early 1990's, did not seem to be widely used or studied since its commercial manufacture began. A new reagent for the problematic and increasingly encountered thermal paper, Thermanin, was also evaluated and compared to other proposed methods for the development of fingerprints on thermal paper. The investigation of 1,2-indanedione as a fingerprint reagent for use in Australia was performed by comparing a number of formulations and development procedures, encompassing all published recommendations as well as some novel approaches. 1,2-indanedione formulations were compared with respect to initial colour, fluorescence, concentration of the reagent, acetic acid concentration and the effect of different carrier solvents. Numerous development conditions were also investigated, including a conventional oven, a heat press and humidity. Further enhancement using metal salts and liquid nitrogen was also evaluated. The heat press set at 165 °C for 10 s proved to give the best initial colour and most intense luminescence. Secondary metal salt treatment improved initial colour and luminescence and was found to provide consistent results despite different environmental conditions. It is for this reason that it is recommended that metal salt treatment consistently be performed after treatment with 1,2-indanedione or included in the formulation of 1,2-indanedione. The Polilight, the VSC 2000, and the Condor Chemical Imaging microscope have been used to detect fingerprints developed with 1,2-indanedione on a variety of high- and low- quality porous and semi-porous surfaces with impressive results overall.

Laboratory and field tests were conducted to compare 1,2-indanedione with DFO and ninhydrin as well as to investigate the position of 1,2-indanedione in the sequence of reagents for fingerprint detection on porous surfaces.

Overall 1,2-indanedione proved to be a viable alternative to tradition methods for the detection of fingerprints on porous surfaces, with more fingerprints being developed using this reagent on real samples than both DFO and ninhydrin and a combination of the two reagents.

The isolation of a single pure product from the reaction of 1,2-indanedione with several different amino acids was not achieved. The study was able to establish that 1,2-indanedione reacts differently with different amino acids with some reactions, such as those with alanine and cysteine, following a similar pathway. A study performed by nuclear magnetic resonance spectroscopy and colour reactions showed that increasing the content of water in the reaction retarded the kinetics of the reaction and thus it is possible that the concentration of water in the reaction may influence the path the reaction takes. Solid state nuclear magnetic resonance spectroscopy indicated that the product of the reaction is ionic, which may help explain the problems encountered on separation and isolation of the product. Thermal and elemental analysis provided some information on the by-products released by the reaction, whilst mass spectroscopy provided information on the possible pathway of the reaction.

The results of this study support the proposal made by Petrovskaja (1999) that the main reaction product of 1,2-indanedione and amino acids is a Ruhemann's purple type product with a molecular mass of 275.

A study of the reaction between metal salts and the 1,2-indanedione/amino acid product was also performed on a crude reaction mixture. This was due to the inability to provide a pure starting materials as well as the unsuccessful separation of the complex by thin layer chromatography. The information gained; however, from a study via nuclear magnetic resonance spectroscopy, mass spectroscopy, UV-visible spectroscopy and infrared spectroscopy indicates that two 1,2-indanedione molecules react with the nitrogen atom in the amino acid forming a tridentate ligand which then complexes with the metal ion. The evaluation of 5-methylthioninhydrin found that the reagent is superior to ninhydrin; however, 1,2-indanedione exhibits much stronger luminescence when used to treat latent

fingermarks. The high cost of the reagent accompanied by the fact that 1,2-indanedione was found to be a superior reagent and is already in use in many laboratories precludes a recommendation for its routine use.

ThermaNin was evaluated against other recommended reagents for the development of fingermarks on thermal paper. ThermaNin itself was found to be extremely sensitive to water and humidity and must be made fresh before its use due to poor stability. Once again a 1,2-indanedione formulation, albeit without acetic acid, was found to be the optimal method to detect fingermarks on this particular surface.

ACKNOWLEDGEMENTS

I would like to thank all of the people who have helped and supported me through the last 6 years that I have been undertaking this project.

Firstly to my supervisors – Professor Chris Lennard, who came up with the idea of the area of research to be performed and for being a constant source of wisdom and advice. I have been honoured to have you as a supervisor. Mr Milutin Stoilovic whose knowledge in the fluorescence and spectroscopy of fingerprints surpasses that of anyone I know. His assistance in these areas of the research has been an enormous support. Finally to Professor Claude Roux, who has been a constant source of encouragement and always made sure I had everything that I needed. Thanks for providing me with some great opportunities through this research, I don't think I would have made it to where I am without that. You challenged me and said a part timer couldn't do it, well I'm glad I have been able to change your mind on that.

Professor Ronald Shimmon who has gone well and beyond the call of his job description and over the last two years has guided me through the organic component of my research. You need a big payrise!!!

To my employer, the New South Wales Police Forensic Services Group who have allowed me study leave and supported my conference visits. To the laboratory staff in particular Senior Sergeant Bob Newell (retired) and Sergeant Zac Ferkula, who were instrumental in introducing 1,2-indanedione into the New South Wales fingerprint laboratory. Thanks also goes to Sergeant Rick Sinclair who helped me with the 1,2-indanedione case examples and had the arduous task of presenting these in court.

To the students who assisted me in this project – Julien Pasquier, Julian Russo and Matthew Thomson-Laing – your work was of great value to me.

To my peers Fiona Burger, Garry Sarkissian and Shaheen Aumeer- Donavan who have made the study time and travel 'almost' enjoyable.

To my family, my mother Sue Wallace and father John Wallace who have encouraged me to achieve the things I wanted in life. My husband and best friend Trevor Kunkel, who puts up with the moods, the stress and picks up a lot of the slack that I leave behind. To my beautiful son Tyson, who if he wasn't such a good baby and toddler I would never have gotten to finish this thesis and my daughter Alyssa for giving me the motivation to finish.

Forewards

CHAPTER 1 – Introduction

Chapter 1 presents an introduction to fingermarks including history, identification, enhancement and detection. It includes an introduction to the reagents used to detect and enhance fingermarks on porous surfaces focusing on ninhydrin, DFO, 1,2-indanedione, 5-methylthioninhydrin and Thermanin, and the previous research conducted into these reagents. A brief outline of the aims of this research is also reported.

CHAPTER 2 – Fingermarks on Porous Surfaces – A Survey

Chapter 2 present a survey which was conducted into the types, formulations and frequency of reagents used to develop fingermark son porous surfaces with the specific aim of gathering information on the awareness, opinion and level of use of the fingermark reagent 1,2-indanedione. The results of the survey are reported and discussed.

Wallace-Kunkel, C., Roux, C., Lennard, C. & Stoilovic, M. (2004) The Detection and Enhancement of Latent Fingermarks on Porous Surfaces - A Survey *Journal of Forensic Identification* 54(6): 687-705

CHAPTER 3 – Optimisation of 1,2-Indanedione

Chapter 3 focused on the investigation of all recommended formulations, development and detection conditions of fingermark treated with 1,2-indanedione. It presents the optimum conditions for the use of the reagent under Australian conditions. Eight formulations in total were investigated as well as novel formulations, the effect of a heat press, a standard oven and added humidity were determined as well as the use of metal salt treatment and cooling with liquid nitrogen. The Polilight, the VSV 2000 and the Condor Chemical Imaging system were all investigated as methods of detection.

Wallace-Kunkel, C., Lennard, C., Stoilovic, M. & Roux, C. (2007) Optimisation and Evaluation of 1,2-Indanedione for use as a Fingermark Reagent and its Application to Real Samples *Forensic Science International* 168: 14-26 **Awarded National Institute of Forensic Science (NIFS) Best Technical Article for 2007**

CHAPTER 4 – Applications of 1,2-Indanedione

In Chapter 4 the formulation of 1,2-indanedione optimised in Chapter 3 is compared with ninhydrin and DFO through the sensitivity of detection of the reagents using amino acids, test samples and through real and randomly laid samples. The position of 1,2-indanedione

in the sequence of reagents for the development of fingermarks on porous surfaces was determined as well as the performance of 1,2-indanedione on difficult porous and semi porous surfaces. A further investigation into the effect of environmental conditions and the effect zinc metal salt is also reported.

Stoilovic, M., Lennard, C., Wallace-Kunkel, C. & Roux, C. (2007) Evaluation of a 1,2-Indanedione Formulation Containing Zinc Chloride for Improved Fingermark Detection on Paper *Journal of Forensic Identification* 57(1): 4-18

CHAPTER 5 – A Study of the 1,2-Indanedione/ Amino Acid Reaction

Chapter 5 reports experiments which aim to gain more insight into the reaction of 1,2-indanedione with amino acids using various instrumental methods including TLC, UV-Vis, IR, NMR, MS, elemental analysis and thermal analysis. A preliminary study into the secondary reaction including metal salts, which had not been previously studied, is also investigated using similar instrumental means.

CHAPTER 6 – Other Reagents for Fingermarks on Porous Surfaces

Chapter 6 presents other applications of 1,2-indanedione as well as investigations into other amino acid specific reagents, 5-methylthioninhydrin and thermanin. 5-Methylthioninhydrin and ThermaNin are two reagents that have been commercially manufactured without a full evaluation of optimum formulation either before manufacture or after. 5-Methylthioninhydrin was evaluated by means of a carrier solvent study, a spectroscopy study, comparison with the conventional reagents, ninhydrin and DFO, and a price comparison.

Thermal paper has often proved problematic for fingermark development. ThermaNin has been recently proposed as a reagent for use on thermal paper. The formulation of ThermaNin was optimised and compared against other proposed reagents for fingermark development on thermal paper such as 1,2-indanedione, ‘Nin-dry’ and a ninhydrin formulation for thermal paper. A novel method for development on fingermarks on thermal paper ‘Ind-dry’ was also proposed and evaluated.

Wallace-Kunkel, C., Lennard, C., Stoilovic, M. & Roux, C. (2006) Evaluation of 5-Methylthioninhydrin for the Detection of Fingermarks on Porous Surfaces and Comparison to Conventional Reagents *Identification Canada* 29(1): 4-13